

[any one of] Claim[s] 1[-14], for use in the manufacture of articles having porous substrates and/or substrates with gaps greater than about 0.5 mils therebetween.

Kindly add new Claim 20 as follows:

20. (New) A photocurable composition comprising:

- (a) a 2-cyanoacrylate component,
- (b) a photoinitiated radical generating component, and
- (c) a photoinitiator component,

wherein the photoinitiated radical generating component includes materials selected from the group consisting of α -haloacetophenones, azo compounds, aromatic carbonyl compounds, peroxides, hydroperoxides, peresters, azoisobutyronitrile, and combinations thereof.

REMARKS

Claims 1-19 were pending in the application.

Applicants have cancelled Claim 8, incorporating the recitations thereof into Claim 1, and added new Claim 20.

Applicants have also amended Claim 7 and the Specification to correct obvious typographical errors.

Replacement Specification pages 3, 4, 11 and 21 and replacement claim pages 28-31, are included herewith.

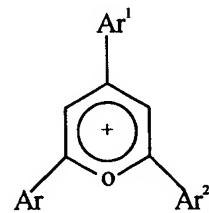
In the Written Opinion, Claims 1-4 and 12 are said to lack novelty under PCT Article 33(2) as allegedly being anticipated by U.S. Patent No. 4,139,388 (Reich) and Claims 15

[sic], 7 and 12 are said to lack novelty under PCT Article 33(2) as allegedly being anticipated by U.S. Patent No. 5,530,037 (McDonnell). In addition, Claims 5-9 are said to lack an inventive step under PCT Article 33(3) as allegedly being obvious over McDonnell. Claims 1-9 are said to lack an inventive step under PCT Article 33(3) as allegedly being obvious over U.S. Patent No. 5,922783 (Wojciak).

Applicants traverse these observations.

For the Authorized Officer's review, Applicants provide a brief description of the invention together with certain salient features thereof.

The present invention is directed to a photocurable composition including a 2-cyanoacrylate component, a photoinitiated radical generating component, and a photoinitiator component. In this composition, the photoinitiated radical generating agent may be selected from α -haloacetophenones, azo compounds, aromatic carbonyl compounds, peroxides, hydroperoxides, peresters, azoisobutyronitrile, and combinations thereof, and the photoinitiator may be selected from compounds within the following structure:



where each of Ar, Ar¹ and Ar² are aryl groups, with or without substitution, and X⁻ is an anion.

Although the predominant mechanism by which cyanoacrylate monomers undergo polymerization is an anionic one (which as noted above is typically initiated using a nucleophile), free-radical polymerization is also known to occur. Free radical polymerization is however seen as troublesome since it tends to reduce shelf-life stability under prolonged exposure to heat or light of an appropriate wavelength. Ordinarily, free-radical stabilizers, such as quinones or hindered phenols, are included in cyanoacrylate-containing adhesive compositions to consume free radicals that are generated by light and under typical non-airtight storage conditions, thereby extending the adhesive's shelf life. Thus, the extent of any free-radical polymerization of commercial cyanoacrylate-containing adhesive compositions is especially undesirable for at least the reason stated and in practice is typically minimal due to the inclusion of such free-radical stabilizers.

Cyanoacrylate-based adhesive compositions have to date not been developed to rapidly cure through a photoinitiated free radical mechanism, while retaining commercially acceptable shelf life stability. Such a composition would be desirable as possessing the benefits and advantages of cyanoacrylate-containing compositions while curing through at least a photo-induced free radical polymerization mechanism.

And reference to the Examples section shows the benefit of using the combination of a photoinitiated radical generating component and a photoinitiator component to achieve that desired result.

As regards the documents cited in the Written Opinion, Applicants provide the following comments to distinguish the invention as presently claimed therefrom.

Reich is directed to phase storage materials for recording spatially modulated optical data. These materials are prepared by introducing p-benzoquinone into cyanoacrylates and polymerizing the cyanoacrylate as a film between two plates. p-Benzoquinone is generally recognized as a free radical scavenger. Reich is silent as to how polymerization occurs in the spatially modulated optical data system. Nevertheless, since p-benzoquinone is a free radical scavenger, it is present with the intention of reacting with free radicals thereby preventing free radicals which form from reacting with other materials.

McDonnell is directed to sterilized cyanoacrylate adhesive compositions that are prepared by exposing the cyanoacrylate to gamma irradiation. The cyanoacrylate is present initially in liquid form and remains in liquid form after exposure to gamma irradiation due to the presence of a stabilizer package, which includes an anionic stabilizer and a free radical stabilizer. The anionic stabilizer is typically sulfur dioxide and the free radical stabilizer is typically a butylated hydroxy anisole, a butyl hydroxy toluene, or

hydroquinones, phenols, and the like.

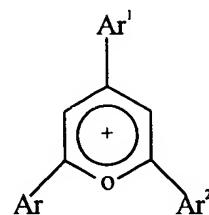
Frankly, Applicants do not see the relevance of sterilization of a liquid composition, which remains liquid after exposure to gamma-irradiation, to a photocurable composition which turns solid after exposure to radiation in the electromagnetic spectrum. One system confers stability, whereas the other confers reactivity.

Like the present invention, Wojciak is also directed to radiation curable cyanoacrylate compositions. Wojciak's compositions include a cyanoacrylate together with a metallocene compound and a photoinitiator component. Thus, instead of Applicants' photoinitiated radical generating component and photoinitiator component combination to achieve photocure of a cyanoacrylate when exposed to the radiation in the electromagnetic spectrum, Wojciak uses the combination of a metallocene component and a photoinitiator component to achieve that result. The difference between the photoinitiated radical generating component and the metallocene component is plain from a review of the respective Specifications.

In contrast to the disclosure, teaching, or suggestion in these three cited patent documents, the present invention is defined by a photocurable composition including:

- (a) a 2-cyanoacrylate component,
- (b) photoinitiated radical generating component,
and
- (c) a photoinitiator component.

The photoinitiated radical generating component includes materials selected from α -haloacetophenones, azo compounds, aromatic carbonyl compounds, peroxides, hydroperoxides, peresters, azoisobutyronitrile, and combinations thereof. And the photoinitiator component includes compounds within the generic structure



The combination of the photoinitiated radical generating component and the photoinitiator component generates radicals that are capable of causing the cyanoacrylate to polymerize under exposure to radiation in the electromagnetic spectrum.

Reich uses benzoquinones, which are known free radical stabilizers, and McDonnell uses a free radical stabilizer, such as butylated hydroxy anisole, a butyl hydroxy toluene, or hydroquinones, phenols, and the like, to stabilize the cyanoacrylate against premature polymerizaiton. That is, these free radical stabilizers perform the exact opposite function than the present invention, which uses the generated free radical in the polymerization of the cyanoacrylate component.

And Wojciak uses a different combination to achieve a photocurable cyanoacrylate.

Accordingly, Applicants believe the claims as amended are in a form that meet all requirements of PCT Article 33, and therefore all objections should be removed.

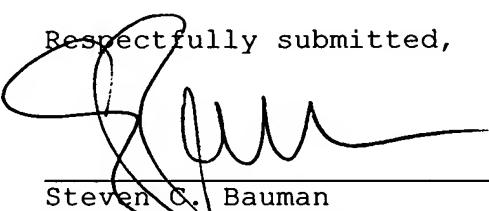
Finally, Claims 13-19 stand objected to under PCT Rules 66.2(a)(b) as allegedly lacking clarity under PCT Article 6.

Accordingly, Applicant's have amended these claims to remove reference to multiple dependency. Thus, each of Claims 13-19 as amended depend from Claim 1.

In view of the above, Applicants respectfully request the issuance of a favorable international preliminary examination report.

Should the Authorized Officer have any questions concerning the amendments set forth above, Applicants' undersigned agent may be reached by telephone at (860) 571-5001, by facsimile at (860) 571-5028, or by email at steve.bauman@loctite.com.

Respectfully submitted,



Steven C. Bauman
Agent for Applicants
Registration No. 33,832

LOCTITE CORPORATION
Legal Department
1001 Trout Brook Crossing
Rocky Hill, CT 06067
USA

Table 1

Sample No.	DBPO [ppm]	TPT [ppm]	After Exposure to 1000 W light [30 secs]
1	0	1000	No curing
2	100	0	No curing
3	500	0	No curing
4	2500	0	No curing
5	10000	0	No curing
6	100	100	High viscous
7	100	1000	Tack-free curing
8	500	100	High viscous
9	500	1000	Tack-free curing
10	2500	100	High viscous
11	2500	1000	Cured
12	10000	100	High viscous
13	10000	1000	High viscous

The information shown in Table 1 indicates that the combination of the radical initiator component and the photoinitiator component (see Sample Nos. 6-13) enables the cyanoacrylate to cure when exposed to UV light, whereas when only one or the other of the radical initiator component or photoinitiator component are present (see Sample Nos. 1-5), no curing of the cyanoacrylate occurs. It may also be seen that vast amounts of the photoinitiated radical generating component is not necessary to observe the behavior of the inventive compositions (see Sample Nos. 6-9).

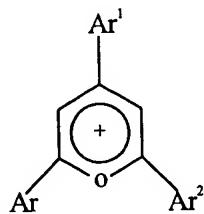
Example 2

In this example, a variety of radical initiator components were used in the formulation.

Again starting with ethyl-2-cyanoacrylate, and keeping the photoinitiator component constant as "TPT", a variety of different radical initiator components were used in the amounts noted to determine whether and to what extent the so-prepared formulations would cure when exposed to UV light. Table 2 below sets forth the specific identity and amounts of the radical initiator components used in the samples. Table 2 also sets forth the curing speed attained in seconds when one drop of the sample was placed on a glass slide (from Smiths Glassware) and exposed to 1000 W of

What Is Claimed Is:

1. A photocurable composition comprising:
 - (a) a 2-cyanoacrylate component,
 - (b) a photoinitiated radical generating component, and
 - (c) a photoinitiator component,
 wherein the photoinitiator component is selected from the compounds within the following structure:



wherein each of Ar, Ar¹ and Ar² are aryl groups, with or without substitution, and X⁻ is an anion.

2. The composition according to Claim 1, wherein the cyanoacrylate component includes a cyanoacrylate monomer represented by H₂C=C(CN)-COOR, wherein R is selected from the group consisting of C₁₋₁₅ alkyl, alkoxyalkyl, cycloalkyl, alkenyl, aralkyl, aryl, allyl and haloalkyl groups.

3. The composition according to Claim 2, wherein the cyanoacrylate monomer is selected from the group consisting of methyl cyanoacrylates, ethyl-2-cyanoacrylate, propyl-2-cyanoacrylates, butyl-2-cyanoacrylates, octyl-2-cyanoacrylates, allyl cyanoacrylate, β -methoxyethyl cyanoacrylates, and combinations thereof.

4. The composition according to Claim 2, wherein the cyanoacrylate monomer is ethyl-2-cyanoacrylate.

5. The composition according to Claim 1, wherein the photoinitiated radical generating component includes materials selected from the group consisting of α -haloacetophenones, azo compounds, aromatic carbonyl compounds, peroxides, hydroperoxides, peresters, azoisobutyronitrile, and combinations thereof.

6. The composition according to Claim 1, wherein the photoinitiated radical generating component includes materials selected from the group consisting of 1,1'-azo-bis(cyclohexanecarbonitrile), 4,4'-azo-bis(4-cyanovaleic acid), 1,1'-(azodicarbonyl)-dipiperidine, 1,1-bis(t-butylperoxy)cyclohexane, 2,5-bis(t-butylperoxy)-2,4-

7. (Amended) The composition according to Claim 1, wherein the photoinitiated radical generating component includes materials selected from the group consisting of 1-hydroxycyclohexyl phenyl ketone, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholino propan-1-one, benzophenone, 2-benzyl-2-N,N'-dimethylamino-1-(4-morpholinophenyl)-1-butanone, 2,2-dimethoxy-2-phenyl acetophenone, bis(2,6-dimethoxybenzoyl-2,4-trimethyl pentyl phosphine oxide, 2,4,6-trimethylbenzoyldiphenyl-phosphine oxide, 2-hydroxy 2-methyl-1-phenyl-propan-1-one, and combinations thereof.

9. The composition according to Claim 1, wherein the photoinitiator component is selected from the group consisting of 2,4,6-triphenylpyrylium tetrafluoroborate, 1,4-phenylene-4,4'-bis-(2,6-diphenyl-4-pyrylium tetrafluoroborate), 2,4-diphenylnaphto-(1,2-B) pyrylium tetrafluoroborate, 2,4,6-triphenyl-pyrylium trifluoromethane sulfonate, 2,6-diphenyl-4(p-tolyl)-pyrylium tetrafluoroborate and combinations thereof.

10. The composition according to Claim 1, further comprising (d) a non-cyanoacrylate radical curable component.

11. The composition according to Claim 8, wherein the non-cyanoacrylate radical curable component is a member selected from the group consisting of styrene and derivatives thereof, (meth)acrylates, and combinations thereof.

12. The composition according to any one of Claims 1-11, wherein radiation in the electromagnetic spectrums appropriate for photocuring the composition is selected from the group consisting of ultraviolet light, visible light, electron beam, x-rays, infrared radiation and combinations thereof.

13. The composition according to Claim 1, further comprising a member selected from the group consisting of viscosity-modifying agents, rubber toughening agents, thixotropy conferring agents, thermal-stabilizing agents, and combinations thereof.

14. The composition according to Claim 1, wherein the composition is useful as an adhesive, a sealant or a coating.

15. A method of polymerizing a photocurable composition, said method comprising the steps of:

(a) providing an amount of the photocurable composition according to Claim 1; and
(b) subjecting the composition to radiation in the electromagnetic spectrum effective to cure the composition.

16. The composition according to Claim 1 in a two-part formulation.

17. The composition according to Claim 1 in a one-part formulation.

18. A composition comprising a reaction product formed from the composition according to Claim 1 after exposure to radiation in the electromagnetic spectrum.

19. The composition according to Claim 1, for use in the manufacture of articles having porous substrates and/or substrates with gaps greater than about 0.5 mils therebetween.

includes monofunctional acrylates and acrylate esters, such as cyano-functionalized acrylates and acrylate esters, examples of which are expressed as 2-cyanoethyl acrylate ($\text{CH}_2=\text{CHCOOCH}_2\text{CH}_2\text{CN}$) and 3-cyanopropyl acrylate ($\text{CH}_2=\text{CHCOOCH}_2\text{CH}_2\text{CH}_2\text{CN}$). (See page 5, lines 19-26.)

5 U.S. Patent No. 4,707,432 (Gatechair) speaks to a free radical polymerizable composition which includes (a) polymerizable partial esters of epoxy resins and acrylic and/or methacrylic, and partial esters of polyols and 10 acrylic acid and/or methacrylic acid, and (b) a photoinitiator blend of a cyclopentadienyl iron complex and a sensitizer or photoinitiator, such as an acetophenone.

15 In C. Katal, P.A. Grutsch and D.B. Yang, "A Novel Strategy for Photoinitiated Anionic Polymerization", Macromolecules, 24, 6872-73 (1991), the authors note that ethyl cyanoacrylate is "unaffected by prolonged (24-h) irradiation with light of wavelength >350 nm" whereas in the presence of NCS^- , cyanoacrylate is observed to solidify immediately, generating heat in the process. Though the 20 NCS^- was not in that case generated as a result of irradiation, it was generated from the Reineckate anion upon ligand field excitation thereof with near-ultraviolet/visible light. See also U.S. Patent Nos. 5,652,280 (Katal) 5,691,113 (Katal) and 5,877,230 (Katal).

25 International Patent Application PCT/US98/03819 describes photocurable compositions including a cyanoacrylate component, a metallocene component and a photoinitiator component.

30 European Patent Publication No. EP 769 721 A1 describes a photocurable compositions of (a) an α -cyanoacrylate and (b) a metallocene compound comprising a transition metal of group VIII of the periodic table and aromatic electron system ligands selected from π -arenes, indenyl, and η -cyclopentadienyl. The photocurable 35 composition may further include (c) a cleavage-type photoinitiator. U.S. Patent No. 5,814,180 (Mikuni) describes such compositions in the context of a method of bonding artificial nails.

describes such compositions in the context of a method of bonding artificial nails.

Although the predominant mechanism by which cyanoacrylate monomers undergo polymerization is an anionic one (which as noted above is typically initiated using a nucleophile), free-radical polymerization is also known to occur. Such free radical polymerization is however seen as troublesome since it tends to reduce shelf-life stability under prolonged exposure to heat or light of an appropriate wavelength. See e.g., Coover et al., supra. Ordinarily, free-radical stabilizers, such as quinones or hindered phenols, are included in cyanoacrylate-containing adhesive compositions to consume free radicals that are generated by light and under typical non-airtight storage conditions, thereby extending the adhesive's shelf life. Thus, the extent of any free-radical polymerization of commercial cyanoacrylate-containing adhesive compositions is especially undesirable for at least the reason stated and in practice is typically minimal due to the inclusion of such free-radical stabilizers.

It is not believed to date that a cyanoacrylate-based adhesive composition has been developed to rapidly cure through a photoinitiated free radical mechanism, while retaining commercially acceptable shelf life stability. Such a composition would be desirable as possessing the benefits and advantages of cyanoacrylate-containing compositions while curing through at least a photo-induced free radical polymerization mechanism.

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SUMMARY OF THE INVENTION

The present invention provides compositions which include a cyanoacrylate component or a cyanoacrylate-containing formulation, a photoinitiated radical generating component and a photoinitiator component. Such compositions cure after exposure to radiation in the electromagnetic spectrum.

The photocurable compositions of this invention retain those benefits and advantages of traditional

applications in which elevated temperature conditions may be experienced, such as with potting compounds particularly where large cure through volume is present and non-tacky surfaces are desirably formed in less than about five
5 seconds.

The inclusion of such materials to a photocurable composition in accordance with the present invention may provide a formulation having particular advantages for certain applications, and should be appealing from a safety
10 perspective as the possibility is decreased of splashing or spilling the composition on exposed skin of the user or bystanders.

Another desirable component to include in the inventive compositions is a photosensitizer to render the composition more reactive toward exposure to electromagnetic radiation. Desirable examples of such photosensitizers include benzophenone or dyes like xanthene dyes, acridinium dyes or phenazine dyes. Inclusion of such photosensitizers often lessens the intensity and/or duration of exposure to
20 the electromagnetic radiation used to initiate cure.

The relative amount of the various components of the photocurable compositions according to this invention is a matter of choice left to those persons of skill in the art, depending of course on the identity of the particular
25 components chosen for a specific composition.

As a general guide, however, it is desirable to include in the photocurable compositions a photoinitiated radical generating component, such as peroxide, perester, azo compounds, benzoin derivatives (e.g., DMPAP), α -halo acetophenones (e.g., DC), acylphosphine oxides (e.g., DPTPO or related phosphine oxide compounds), in an amount within the range of about 0.005% to about 4% or greater (desirably within the range of about 0.01% to about 1.5%) by weight of the total composition. It is also desirable for the compositions to include a photoinitiator component, such as substituted pyrylium salts or anthracene and derivatives thereof, e.g., substituted anthracenes, or anthraquinone or